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(19)

(72) Inventor JURGEN SCHWINDT

(54) A CATALYST COMBINATION FOR THE ISOCYANATE POLYADDITION REACTION

(71) We, BAYER AKTIENGESELLSCHAFT, a body corporate organised under the laws of Germany, of 509 Leverkusen, Germany; do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a catalyst combination for the isocyanate polyaddition reaction.

It has been known for some time that numerous heavy metal compounds and amines are effective catalysts for isocyanate addition reactions (*cf.* K. C. Frisch, L. P. Rennao "Catalysis in Isocyanate Reactions" in J. Macromol. Sci.-Revs. Macromol. Chem. C5 (1), 103—150 (1970)).

In addition, it is known that combinations of metal compounds and amines have a synergistic effect which may be commercially utilised, particularly in the reaction of polyisocyanates with polyols (*cf.* J. H. Saunders and K. C. Frisch, Polyurethanes, Part I, Interscience Publishers, New York—London—Sydney, 1962, pages 231—232).

Catalytically the most active amines, which generally contain tertiary-bonded nitrogen, for example 1,4-diaza-bicyclo-(2,2,2)-octane, generally have to be used in concentrations of from 0.04 to 0.5 part, by weight, based on the polyol used, while in the case of other amines or in cases where it is desired to catalyse reactions of aliphatic isocyanates considerably larger quantities have to be used.

However, even the use of small quantities of amine catalysts involves serious disadvantages. Since the commercially used catalysts are generally tertiary amines which are not chemically incorporated in the polyurethane, an unpleasant amine odour continues to be given off some considerable time after production of the polyurethane plastic. This odour is particularly unpleasant in the case of articles in everyday use, such as upholstered goods, motor vehicle trim, shoes and furniture.

In many cases, the amines also result in a yellowing of light-coloured leather or plastics surfaces.

The use of bicyclic amidines as polyurethane catalysts is described in German Offenlegungsschrift No. 1,745,418, in which the use of organometallic compounds is also mentioned. The use of free amidines as catalysts for reactions of aliphatic isocyanates is described in German Offenlegungsschrift No. 1,950,262. Unfortunately, compounds of this type have the disadvantage that they are readily decomposed by water (*cf.* Houben-Weyl-Müller, Methoden der organischen Chemie, Published by G. Thieme, Stuttgart, Vol. XI, page 940).

This largely precludes the use of such catalysts for foam systems where water is used as the blowing agent. Similarly, the traces of water which are always present in polyols are sufficient to reduce the catalytic activity of free amidines within the matter

of days. Accordingly, a polyol mixture containing an amidine catalyst may only be stored for a limited period.

In the same way as water, numerous halogenated hydrocarbons, such as methylene chloride, chloroform, carbon tetrachloride, dichloroethylene, trichloroethylene and ethylene dichloride, seriously restrict the potential application of amidines. They react very quickly by quaternisation, as a result of which the amidines become substantially ineffectual as catalysts.

The present invention relates to the use of certain hydrazines as co-catalysts for the isocyanate polyaddition reaction. Together with certain metal compounds, they form excellent catalyst systems which do not have any of the disadvantages referred to above and, in particular, show the following advantages:

1. Foams produced using the present catalyst combinations do not have any noticeable odour because the hydrazines used react with isocyanates to form the semi-carbazide.
2. In contrast to the amidines, the hydrazine compounds used in accordance with the present invention may be stored in the presence of water and halogenated hydrocarbons.
3. In the production of plastics foamed in moulds, the present catalyst systems provide for easier mould release. In this respect they are distinguished with particular advantage from the combinations of 1,4 - diazabicyclo - (2,2,2)-octane and organic tin(IV) compounds hitherto preferably used as catalyst.

The present invention relates to a catalyst combination for the isocyanate polyaddition reaction consisting of:

(A) 1 mole of a metal compound corresponding to the following general formula:

$$Me\ X_n\ Y_m$$

wherein

Me represents an $(n+m)$-valent metal, preferably selected from Cu, Ag, Au, Zr, Cd, Hg, Mr, Re, Fe, Co, Ni, Ge, Sr and Pb;

X represents an aliphatic hydrocarbon radical preferably having from 1 to 18 carbon atoms, an aromatic hydrocarbon radical preferably having from 6 to 10 carbon atoms or an araliphatic hydrocarbon radical preferably having from 7 to 15 carbon atoms;

Y represents an aliphatic carboxylate radical preferably having from 2 to 18 carbon atoms which may contain one or more olefinic double bonds and/or alcoholic hydroxyl groups, an enolate radical preferably having from 5 to 18 carbon atoms, salicylate or naphthenate;

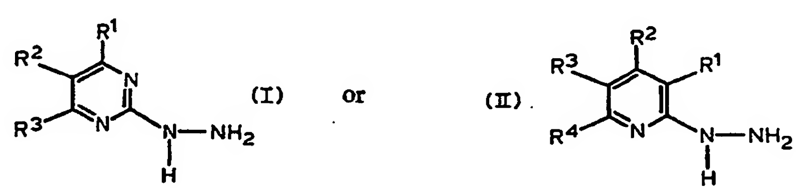
n represents 0, 1 or 2; and

m represents 0 or an integer of from 1 to 4; with the proviso that the sum $(n+m)$ is 2, 3 or 4; and

(B) from 0.5 to 6 moles of a heterocyclic aromatic compound which contains at least one tertiary nitrogen atom as hetero-atom and which has at least one hydrazino substituent, preferably in the ortho- or para-position to the hetero-atom.

In the heterocyclic aromatic compounds, poor in π-electrons, used as co-catalysts in accordance with the present invention, the reactivity of the hydrazine group is weakened as a result of the electronegativity of the aromatic nucleus increased by the tertiary nitrogen atom. Co-catalysts preferably used in accordance with the present invention, are the following:

(1). Hydrazines corresponding to one of the following general formulae:

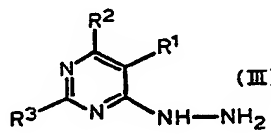
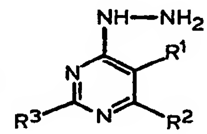


wherein

R^1, R^2, R^3 and R^4 which may be the same or different, each represents hydrogen, a hydroxyl, nitro or cyano group, an aliphatic hydrocarbon radical preferably having from 1 to 6 carbon atoms or an aromatic hydrocarbon radical preferably having from 6 to 12 carbon atoms. R^2 and R^3 or R^1 and R^2 or R^3 and R^4 may also represent a condensed ring so that corresponding bicyclic and tricyclic aromatic compounds are formed.

The following are examples of hydrazines of this type: 2 - hydrazinopyrimidine, 4 - hydroxy - 2 - hydrazino - 6 - methyl pyrimidine, 2 - hydrazinopurine, 2 - hydrazinopyridine, 2 - hydrazinoquinoline, 5 nitro - 2 - hydrazinopyrimidine and 2 - hydrazino - 6 - methyl pyrimidine.

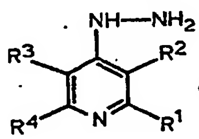
(2). Hydrazines corresponding to one of the following general formulae:


(III) or (IV)


wherein
R^1, R^2 and R^3 are as defined above.

The following are examples of hydrazines of this type: 4 - hydrazinopyrimidine, 4 - hydrazino - 6 - methyl pyrimidine, 4 - hydrazino - 6 - phenyl pyrimidine and 6-hydrazino - 2,5 - diphenyl cyanopyrimidine.

(3). Hydrazines corresponding to one of the following general formulae: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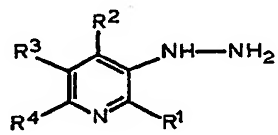
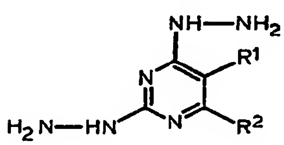

(VI)

wherein
R^1, R^2, R^3 and R^4 are as defined above.

The following are examples of hydrazines of this type: 3 - hydrazinopyridine, 4 - hydrazinopyridine, 4 - hydrazinomethyl quinoline, 2 - ethyl - 3 - hydrazinopyridine and 4 - hydrazinoquinoline.

(4). Hydrazines corresponding to one of the following general formulae: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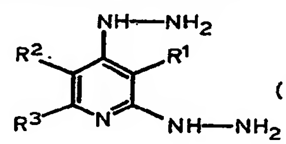
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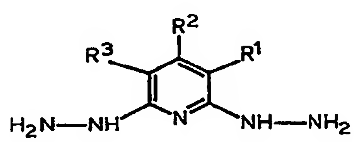
or

(IX)

wherein
R^1, R^2 and R^3 are as defined above.

The following are examples of hydrazines of this type: 2,6 - dihydrazinopyrimidine, 2,6 - dihydrazinopurine, 2,6 - dihydrazino - 3,5 - diphenyl pyrimidine, 2,4 - dihydrazinopyridine, 2,6 - dihydrazinopyridine and the 2,4- and 2,6 - dihydrazinopicolines.

It is particularly preferred to use those compounds corresponding to above general formulae I to IX wherein R^1, R^2, R^3 and R^4 each represents hydrogen or only one of the radicals R^1 to R^4 represents methyl whilst each of the others represents hydrogen or two of the radicals R^1 to R^4 represents a condensed aromatic ring whilst each of the others represents hydrogen.

The dihydrazino compounds are of particular interest because they have a chain-extending effect in the reaction mixture even at low temperatures (by reaction with polyisocyanates to form bis-semicarbazides). In contrast to the corresponding amino compounds, however, the monohydrazine derivatives used in accordance with the present invention do not represent chain-terminators because they are bifunctional with respect to isocyanates at elevated temperatures.

The fact that the co-catalysts according to the present invention, which contain at least one primary, at least one secondary and at least one tertiary amino group, show surprising catalytic activity in combination with metal compounds becomes clear

when the activity of the above hydrazine compounds is compared with phenyl hydrazine or nitrophenyl hydrazine in combination with metal catalysts.

In the latter two cases, the mixtures tested do not show any distinct increase in catalytic activity in relation to the metal compound on its own.

According to the present invention, metal compound of trivalent iron, divalent nickel, divalent zinc, trivalent manganese, divalent tin and tetravalent tin, are preferably used in combination with the above amines. The following are examples of suitable metal compounds: Fe(III)acetate, Fe(III)oleate, Fe(III)stearate, Fe(III)acetyl acetonate; Zn-acetate, Zn-oleate, Zn-acetyl acetonate; Mn(II)acetate, Mn(II)acetyl acetonate, Mn(II)palmitate, Mn(II)versatate ("Versatic" is a Registered Trade Mark), Mn(II)naphthenate; Sn(II)acetate, Sn(II)octoate, Sn(II)isooctoate, Sn(II)ricinoleate, Sn(II)naphthenate; dibutyl-Sn(IV)dilaurate, dibutyl-Sn(IV)octoate, diethyl-Sn(IV)-2-methyl hexoate, diphenyl-Sn(IV) caproate; Ni(I)ricinoleate; Ni(II)acetate, Ni(II)octoate, Ni(II)oleate, Ni(II)acetyl acetonate and Ni(II)salicylate.

According to the present invention, the described hydrazines and the metal compounds are used in a molar ratio of hydrazine compound to metal compound of from 0.5:1 to 6:1.

In flexible-foam formulations, it is preferred to use larger quantities of the hydrazine compound (e.g. molar ratio from 3:1 to 6:1), while in the production of rigid and semi-rigid foams the components of the catalyst combinations according to the present invention are used in substantially equimolar quantities. The hydrazine compound forms with the metal compound an isolatable complex in a molar ratio of 1:1 which may be established by thin-layer chromatography and NMR- and IR-spectroscopy.

The complexes may be produced, for example, by mixing the components in low molecular weight alcohols, such as tetraethylene glycol or trimethylol propane, at temperatures of from 50 to 100°C. After cooling to room temperature, the complex, an oil, separates from the alcohol and may be isolated by means of a separating funnel.

It is, of course, also possible to mix the components in a low-boiling inert organic solvent, such as acetone, diethyl ether, methanol, ethanol, toluene or xylene, and to isolate the complex by evaporating off the solvent.

The complexes may also be directly produced in high molecular weight polyols of the type used for isocyanate polyaddition reactions. The complexes do not separate off from these solutions. The dissolved complexes show similar catalytic activity to the pure complexes.

The catalyst combinations according to the present invention may be added to the reaction mixtures to be catalysed in the form of the separate individual components, in the form of the preformed complex which may be mixed with additional hydrazine compound or metal compound or preferably in solution in relatively high molecular weight polyols.

Where the present combinations are used in accordance with the present invention, preferably from 0.001 to 4%, by weight, more preferably from 0.01 to 0.8%, by weight, of the catalyst combination is normally added to the polyol component used for producing the polyurethane plastics.

The present catalyst combinations may be used with advantage both in the production of solid elastomers and also for the production of polyurethane foams. Rigid, semi-rigid or flexible products may be produced in accordance with the present invention depending upon formulation and procedure. The densities are variable generally from 15^3 to 1000 kg/m³.

Surprisingly, the semicarbazides obtained by reaction of the hydrazines with isocyanates also show favourable catalytic activity in combination with the organometallic compounds.

In addition to the catalytic activity thereof, the dihydrazine compounds are also of interest as hydrazine cross-linkers and are therefore used with advantage as chain-extenders in even larger concentrations than those described above.

Accordingly, the present invention also relates to a process for the production of a polyurethane plastics by reacting a polyisocyanate, a relatively high molecular weight compound containing at least two isocyanate-reactive hydrogen atoms and, optionally, a chain-extender in the presence of a catalyst combination according to the present invention.

Starting components suitable for use in accordance with the present invention include: aliphatic, cycloaliphatic, araliphatic, aromatic and heterocyclic polyisocyanates of the type described, for example, by W. Siefken in Justus Liebigs Annalen der Chemie, 562, pages 75 to 136, for example ethylene diisocyanate; 1,4 - tetramethylene diisocyanate; 1,6 - hexamethylene diisocyanate; 1,12 - dodecane diisocyanate;

cyclobutane - 1,3 - diisocyanate; cyclohexane - 1,3 - and 1,4 - diisocyanate and mixtures of these isomers; 1 - isocyanato - 3,3,5 - trimethyl - 5 - isocyanatomethyl cyclohexane as described in German Auslegeschrift No. 1,202,785 and U.S. Patent No. 3,401,190; 2,4- and 2,6 - hexahydrotolylene diisocyanate and mixtures of these isomers; hexahydro - 1,3- and/or 1,4 - phenylene diisocyanate; perhydro - 2,4'- and/or -4,4' - diphenylmethane diisocyanate; 1,3- and 1,4 - phenylene diisocyanate; 2,4- and 2,6 - tolylene diisocyanate and mixtures of these isomers; diphenyl methane - 2,4' and/or -3,4' - diisocyanate; naphthylene - 1,5 - diisocyanate; triphenylmethane - 4,4',4''-triisocyanate; polyphenyl polymethylene polyisocyanates of the type which may be obtained by condensing aniline with formaldehyde, followed by phosgenation, and which are described, for example, in British Patent Nos. 874,430 and 848,671; *m*- and *p*-isocyantophenyl sulphonyl isocyanates according to U.S. Patent No. 3,454,606; perchlorinated aryl polyisocyanates of the type described, for example, in U.S. Patent No. 3,277,138; polyisocyanates containing carbodiimide groups of the type described in U.S. Patent No. 3,152,162; diisocyanates of the type described in U.S. Patent No. 3,492,330; polyisocyanates containing allophanate groups of the type described, for example, in British Patent No. 994,890; Belgian Patent No. 761,626 and published Dutch Patent Application No. 7,102,524; polyisocyanates containing isocyanurate groups of the type described, for example, in U.S. Patent No. 3,001,973; German Patent Nos. 1,022,789; 1,222,067 and 1,027,394; and German Offenlegungsschrift Nos. 1,929,034 and 2,004,048; polyisocyanates containing urethane groups of the type described, for example, in Belgian Patent No. 752,261 or in U.S. Patent No. 3,394,164; polyisocyanates containing acylated urea groups according to German Patent No. 1,230,778; polyisocyanates containing biuret groups of the type described, for example, in German Patent No. 1,101,394 U.S. Patent Nos. 3,124,605 and 3,201,372 and in British Patent No. 889,050; polyisocyanates obtained by telomerisation reactions of the type described, for example, in U.S. Patent No. 3,654,106; polyisocyanates containing ester groups of the type described, for example, in British Patent Nos. 965,474 and 1,072,956; U.S. Patent No. 3,567,763 and German Patent No. 1,231,688; also reaction products of the above-mentioned isocyanates with acetals according to German Patent No. 1,072,385 and polyisocyanates containing polymeric fatty acid radicals according to U.S. Patent No. 3,455,883.

It is also possible to use the isocyanate group-containing distillation residues accumulating in the production of isocyanates on a commercial scale, optionally in solution in one or more of the aforementioned polyisocyanates. It is also possible to use mixtures of the aforementioned polyisocyanates.

In general, it is particularly preferred to use the commercially readily available polyisocyanates, for example 2,4- and 2,6-tolylene diisocyanate, also mixtures of these isomers ("TDI"), polyphenyl polymethylene polyisocyanates of the type obtained by condensing aniline with formaldehyde, followed by phosgenation ("crude MDI") and polyisocyanates containing carbodiimide groups, urethane groups, allophanate groups, isocyanurate groups, urea groups or biuret groups ("modified polyisocyanates").

Other starting components for the production of polyurethane plastics using the present catalyst combinations in accordance with the present invention are compounds containing at least two isocyanate-reactive hydrogen atoms and generally having a molecular weight of from 400 to 10,000. In addition to compounds containing amino groups, thiol groups or carboxyl groups, compounds of this type are preferably polyhydroxyl compounds, more especially compounds containing from 2 to 8 hydroxyl groups, particularly those having molecular weights of from 800 to 10,000 preferably from 1000 to 6000, for example polyesters, polyethers, polythioethers, polyacetals, polycarbonates, polyamides and polyester amides containing at least 2, generally from 2 to 8, but preferably from 2 to 4 hydroxyl groups, of the type known for the production of non-cellular and cellular polyurethanes.

Examples of suitable polyesters containing hydroxyl groups are reaction products of polyhydric, preferably dihydric, and optionally, trihydric alcohols with polybasic, preferably dibasic carboxylic acids. Instead of the free polycarboxylic acids, the corresponding polycarboxylic acid anhydrides or corresponding polycarboxylic acid esters of lower alcohols or mixtures thereof may also be used for the production of the polyesters. The polycarboxylic acids may be aliphatic, cycloaliphatic, aromatic and/or heterocyclic and may optionally be substituted one or more times, for example by halogen atoms, and/or may be unsaturated. Examples of these reactants are: succinic acid; adipic acid; suberic acid; azelaic acid; sebacic acid; phthalic acid; isophthalic acid; trimellitic acid; phthalic acid anhydride; tetrahydrophthalic acid anhydride; hexahydrophthalic acid anhydride; tetrachlorophthalic acid; anhydrophthalic acid anhydride; glutaric acid anhydride; maleic acid; maleic acid anhydride; fumaric acid;

dibasic and tribasic fatty acids, which may be used in admixture with monobasic fatty acids such as oleic acid; terephthalic acid dimethyl ester; and terephthalic acid-bis-glycol ester. Examples of suitable polyhydric alcohols are: ethylene glycol; 1,2- and 1,3-propylene glycol; 1,4- and 2,3-butylene glycol; 1,6-hexane diol; 1,8-octane diol; neopentyl glycol; cyclohexane dimethanol(1,4-bis-hydroxy methyl cyclohexane); 2-methyl-1, 3-propane diol; glycerol; trimethylol propane; 1,2,6-hexane triol; 1,2,4-butane triol; trimethylol ethane; pentaerythritol; quinitol; mannitol; sorbitol; methyl glycoside; also diethylene glycol; triethylene glycol tetraethylene glycol; dibutylene glycol and higher polybutylene glycols. The polyesters may contain terminal carboxyl groups. Polyesters of lactones, for example ε-caprolactone, or of hydroxy carboxylic acids, for example ω-hydroxy caproic acid, may also be used.

The polyethers containing at least two, generally from two to eight, preferably two or three, hydroxyl groups which may be used in accordance with the present invention are also known and are obtained, for example, by the polymerisation of epoxides, such as ethylene oxide, propylene oxide, butylene oxide, tetrahydrofuran, styrene oxide or epichlorhydrin, on their own, for example in the presence of boron trifluoride, or by the chemical addition of these epoxides, either in admixture or successively, to starter components containing reactive hydrogen atoms, such as water, ammonia, alcohols or amines, for example ethylene glycol, 1,3- or 1,2-propylene glycol, trimethylol propane, 4,4′-dihydroxy diphenyl propane, aniline, ethanolamine and ethylene diamine. According to the present invention, it is also possible to use sucrose polyethers of the type described, for example in German Auslegeschrift Nos. 1,176,358 and 1,064,938. In many cases, it is preferred to use polyethers of the type which predominantly contain primary hydroxyl groups (up to 90% by weight, based on all the hydroxyl groups present in the polyether). Polyethers modified by vinyl polymers of the type obtained, for example, by the polymerisation of styrene and acrylonitrile in the presence of polyethers (U.S. Patent Nos. 3,383,351; 3,304,273; 3,523,093 and 3,110,695 and German Patent No. 1,152,536) are also suitable. Polybutadienes containing hydroxyl groups are also suitable.

Among the polythioethers, reference is made in particular to the condensation products of thiodiglycol with itself and/or with other glycols, dicarboxylic acids, formaldehyde, aminocarboxylic acids or amino alcohols. Depending upon the co-components, these products are polythio ethers, polythio mixed ethers, polythioether esters, polythioether ester amides and mixed polyaminothio ethers.

Suitable polyacetals are, for example, those compounds which may be obtained from the reaction of glycols, such as diethylene glycol, triethylene glycol, 4,4′-dioxethoxy diphenyl dimethyl methane and hexane diol, with formaldehyde. Polyacetals suitable for the purposes of the present invention may also be obtained by polymerising cyclic acetals.

Suitable polycarbonates containing hydroxyl groups are those known compounds which are obtainable, for example, by reacting diols, such as 1,3-propane diol; 1,4-butane diol and/or 1,6-hexane diol; diethylene glycol; triethylene glycol or tetraethylene glycol, with diaryl carbonates, for example diphenyl carbonate, or with phosgene.

Examples of the polyester amides and polyamides are the predominantly linear condensates obtained from polybasic saturated and unsaturated carboxylic acids or the anhydrides thereof and polyfunctional saturated and unsaturated amino alcohols, diamines, higher polyamines and mixtures thereof.

Polyhydroxyl compounds already containing urethane or urea groups which may be mixed with modified natural polyols, such as castor oil and carbohydrates, such as starch, may also be used. Addition products of alkylene, oxides with phenol/formaldehyde resins or even with urea/formaldehyde resins may also be used in accordance with the present invention.

Representatives of these compounds used in accordance with the present invention are described, for example, in High Polymers, Vol. XVI, "Polyurethanes, Chemistry and Technology", by Saunders-Frisch, Interscience Publishers, New York, London, Vol. I, 1962, pages 32 to 42 and pages 44 to 54, and Vol. II, 1964, pages 5—6 and 198—199, and in Kunststoff-Handbuck, Vol. VII, Vieweg-Hochtlen, Carl-Hanser-Verlag, Munich, 1966, for example on pages 45 to 71.

It is, of course, possible to use mixtures of the above-mentioned compounds containing at least two isocyanate-reactive hydrogen atoms and generally having a molecular weight of from 400 to 10,000, for example mixtures of polyethers and polyesters.

Other starting compounds which may be used in accordance with the present invention are compounds containing at least two isocyanate-reactive hydrogen atoms

and having a molecular weight of from 32 to 400. In this case, too, compounds of this type are compounds containing hydroxyl groups and/or amino groups and/or thiol groups and/or carboxyl groups, preferably compounds containing hydroxyl groups and/or amino groups which are used as chain-extending or cross-linking agents. These compounds generally contain from 2 to 8 isocyanate-reactive hydrogen atoms, preferably 2 or 3 such hydrogen atoms. The following are mentioned as examples of such compounds: ethylene glycol; 1,2- and 1,3-propylene glycol; 1,4- and 2,3-butylene glycol; 1,5-pentane diol; 1,6-hexane diol; 1,8-octane diol; neopentyl glycol; 1,4-bis-hydroxymethyl cyclohexane; 2-methyl-1,3-propane; glycerol; trimethylol propane; trimethylol ethane; 1,2,6-hexane triol; pentaerythritol; quinitol; mannitol; sorbitol; diethylene glycol; triethylene glycol; tetraethylene glycol; higher polyethylene glycols having a molecular weight of up to 400; dipropylene glycol; higher polypropylene glycols having a molecular weight of up to 400; dibutylene glycol; higher polybutylene glycols having a molecular weight of up to 400; 4,4′-dihydroxy diphenyl propane; dihydroxy methyl hydroquinone; ethanolamine; diethanolamine; triethanolamine; 3-aminopropanol; ethylene diamine; 1,3-diaminopropane; 1-mercapto-3-aminopropane; 4-hydroxy- or amino-phthalic acid; succinic acid; adipic acid; hydrazine; N,N′-dimethyl hydrazine and 4,4′-diamino-diphenyl methane.

In this case, too, it is possible to use mixtures of different compounds containing at least two isocyanate-reactive hydrogen atoms and having a molecular weight of from 32 to 400.

The production of polyurethane plastics using the catalyst combinations in accordance with the present invention, is often carried out using water and/or readily volatile organic substances as blowing agents. Suitable organic blowing agents are, for example, acetone; ethyl acetate; vinylidene chloride; halogen-substituted alkanes, such as methylene chloride; chloroform; ethylidene chloride; monofluorotrichloromethane, chlorodifluoromethane and dichlorodifluoromethane; or butane; hexane; heptane or diethyl ether. A blowing effect may also be obtained by adding compounds which decompose at temperatures above room temperature giving off gases, for example nitrogen, for example azo compounds, such as azoisobutyronitrile. Other examples of blowing agents and information of the use of blowing agents may be found in Kunststoff-Handbuch, Vol. VII, by Vieweg und Hochtlen, Carl-Hanser-Verlag, Munich, 1966, for example on pages 108 and 109, 453 to 455 and 507 to 510.

It is, of course, also possible to use other catalysts in addition to the catalyst combinations according to the present invention, above all in cases where particular effects may be obtained by so doing.

Examples of suitable known co-catalysts are, for example, tertiary amines, such as triethyl amine; tributyl amine; N - methyl morpholine; N - ethyl morpholine; N-cocomorpholine; N,N,N′,N′ - tetramethyl ethylene diamine; 1,4 - diazabicyclo-(2,2,2) - octane; N - methyl - N′ - dimethyl aminoethyl piperazine; N,N - dimethyl benzylamine; bis - (N,N - diethylaminoethyl) - adipate; N,N - diethyl benzylamine; pentamethyl diethylene triamine; N,N - dimethyl cyclohexylamine; N,N,N′,N′ - tetramethyl - 1,3 - butane diamine; N,N - dimethyl - β - phenyl ethylamine; 1,2 - dimethyl imidazole and 2 - methyl imidazole. Other suitable catalysts are known Mannich bases of secondary amines, such as dimethylamine, and aldehydes, preferably formaldehyde, or ketones, such as acetone, methyl ethyl ketone and cyclohexanone, and phenols, such as phenol, nonylphenol or bis-phenol.

Examples of tertiary amine catalysts containing isocyanate reactive hydrogen atoms are triethanolamine; triisopropanolamine; N-methyl diethanolamine; N-ethyl diethanolamine; N,N - dimethyl ethanolamine and also the reaction products thereof with alkylene oxides, such as propylene oxide and/or ethylene oxide.

Other suitable co-catalysts are silaamines having carbon-silicon bonds of the type described, for example, in U.S. Patent No. 3,620,984, for example 2,2,4 - trimethyl-2 - silamorpholine or 1,3 - diethyl aminomethyl tetramethyl disiloxane.

Other suitable co-catalysts are nitrogen-containing bases, such as tetraalkyl ammonium hydroxides, also alkali metal hydroxides, such as sodium hydroxide, alkali metal phenolates, such as sodium phenolate, or alkali metal alcoholates, such as sodium methylate. Hexahydrotriazines may also be used as catalysts.

It is, of course, also possible to use mixtures of different catalyst combinations according to the present invention or to add other organometallic components in cases where known reactions are additionally catalysed in this way, for example dimerisation, trimerisation or carbodiimide formation of the isocyanates, or even when further reactions may be catalysed in this way, such as allophanate formation or biuret formation.

The additional catalysts may be used in quantities of from 0 to 90%, by weight, of the catalyst total, preferably in quantities of from 0 to 50%, by weight.

The production of polyurethane plastics using the catalyst combinations according to the present invention may also be carried out in the presence of surface-active additives (emulsifiers and/or foam stabilisers).

Examples of emulsifiers are the sodium salts of castor oil sulphonates or salts of fatty acids with amines, such as diethylamine/oleic acid or diethanolamine/stearic acid. Alkali metal or ammonium salts of sulphonic acids, such as those of dodecyl benzene sulphonic acid or dinaphthyl methane disulphonic acid or of fatty acids, such as ricinoleic acid, or of polymeric fatty acids, may also be used as surface-active additives.

Suitable foam stabilisers are above all polyether siloxanes, especially water-soluble types. These compounds are generally of such structure that a copolymer of ethylene oxide and propylene oxide is attached to a polydimethyl siloxane radical. Foam stabilisers of this type are described, for example, in U.S. Patent Nos. 2,834,748; 2,917,480 and 3,629,308.

According to the present invention, it is also possible to use reaction retarders, for example substances which are acid in reaction, such as hydrochloric acid or organic acid halides, also known cell regulators, such as paraffins or fatty alcohols or dimethyl polysiloxanes, as well as pigments or dyes and known flameproofing agents, for example tris-chloroethyl phosphate, tricresyl phosphate or ammonium phosphate and polyphosphate, also stabilisers against the effects of ageing and weather, plasticisers and substances having fungistatic and bacteriostatic effects and fillers, such as barium sulphate, kieselguhr, carbon black or prepared chalk.

Other examples of the surface-active additives and foam stabilisers which may be used in accordance with the present invention and of cell regulators, reaction retarders, stabilisers, flameproofing substances, plasticisers, dyes, fillers and substances having fungistatic and bacteriostatic effects, and also details on the way in which these additives are to be used and how they work, may be found in Kunststoff-Handbuch, Vol. VII, published by Vieweg and Hochtlen, Carl-Hanser-Verlag, Munich, 1966, for examples on pages 103 to 113.

According to the present invention, the reaction components may be reacted by the known single-stage process, by the prepolymer process or by the semi-prepolymer process, in many cases using machines of the type described, for example in U.S. Patent No. 2,764,565. Particulars of processing equipment suitable for use in accordance with the present invention may be found, for example, on pages 121 and 205 of Kunststoff-Handbuch, Vol. VII, published by Vieweg und Hochtlen, Carl-Hanser-Verlag, Munich, 1966.

In the production of foams, the foaming reaction is preferably carried out in moulds in accordance with the present invention. To this end, the reaction mixture is introduced into a mould. Suitable mould materials are metals, for example aluminium, or plastics, for example epoxide resins. Inside the mould the foamable reaction mixture foams and forms the moulding. In-mould foaming may be carried out in such a way that the moulding has a cellular structure at its surface, or even in such a way that the moulding has a compact skin and a cellular core. According to the present invention, it is possible in this connection to introduce such a quantity of foamable reaction mixture into the mould that the foam formed just fills the mould. However, it is also possible to introduce into the mould more foamable reaction mixture than is required for filling the mould with foam. This technique is known as "overcharging" and is known, for example, from U.S. Patent Nos. 1,178,490 and 3,182,104.

Known "external release agents", such as silicone oils, are frequently used for in-mould foaming. However, it is also possible to use so-called "internal release agents", which may be used in admixture with external release agents, such as are known, for example, from German Offenlegungsschrift Nos. 2,121,670 and 2,307,589.

According to the present invention, it is also possible to produce cold-hardening foams (British Patent No. 1,162,517 and German Offenlegungsschrift No. 2,153,086).

However, it is, of course, also possible to produce foams by block foaming or by the known laminator process.

The present invention is illustrated by the following Examples in which the figures quoted represent parts, by weight, and percentages, by weight, unless otherwise indicated.

EXAMPLE 1

11 g (0.1 mole) of 2-hydrazinopyrimidine are introduced into 100 ml of tetraethylene glycol, followed by the addition of 63 g (0.1 mole) of dibutyl tin dilaurate.

The mixture is stirred for 10 minutes at from 50 to 100°C and then cooled. An oil separates off from the solvent.

The oil is examined by thin layer chromatography (silica gel; eluent ether; colouring using sulphuric acid). The chromatogram contains only one spot. For comparison, separate solutions of hydrazinopyrimidine and dibutyl tin dilaurate are applied and similarly treated. Two spots are obtained after colouring using sulphuric acid.

EXAMPLE 2

Semi-rigid free-foamed polyether foam having a density of approximately 400 mg/cm^3.

The symbols used have the following meaning:

T_1=beginning of the blowing reaction,
T_2=end of the blowing reaction,
T_3=absence of tack
T_4=hardening time (after this time it is no longer possible to tear out parts of the foam by hand).

Formulation:

70 g of bifunctional propylene-glycol-started polyether of 90% of propylene oxide and 10% of ethylene oxide (hydroxyl number 27.5),

20 g of trifunctional trimethylol-propane-started polyether (hydroxyl number 35.4) of 90% of propylene oxide and 10% of ethylene oxide,

8 g of 1,4-butane diol, 12 g of trifluorochloromethane, 0.06 g of catalyst complex (2-hydrazinopyrimidine/dibutyl tin dilaurate in a molar ratio of 1:1).

The components are carefully mixed for 30 seconds at room temperature using a high speed stirrer, after which 76.7 g of 4,4'-diisocyanatodiphenyl methane are added and the mixture stirred for another 15 seconds.

T_1=30±3 seconds
T_2=48±3 seconds
T_3=48±3 seconds
T_4=58±5 seconds

EXAMPLE 3 (Comparison Test)

By way of comparison, the same foam formulation is catalysed using triethylene diamine and dibutyl tin dilaurate, 0.06 g of catalyst mixture (molar ratio 1:1) again being used.

T_1=55±5 seconds
T_2=T_3=100±10 seconds
T_4=140±10 seconds

EXAMPLE 4

When a mixture of the following components is processed by the same procedure as in Example 2:

75.6 g. of a polyisocyanate (reaction product of 5 mol of 4,4' - diphenylmethane diisocyanate and 1 mol of tripropylene glycol) having an NCO content of 22.6%;
90 g of a polyester polyol (hydroxyl number 55) of adipic acid, 1,4-butane diol and ethylene glycol;
14 g of 1,4-butane diol;
0.2 g of 2-hydrazinopyrimidine/dibutyl tin dilaurate (molar ratio 1:1) and
0.4 g of water,

the following reaction profile is obtained:

T_1=20 seconds
T_2=32 seconds
T_3=65 seconds
T_4=70 seconds

EXAMPLE 5 (Comparison Test)

The procedure of Example 4 is repeated using 1,4-diaza-bicylco-(2,2,2)-octane (DABCO Registered Trade Mark). In order to obtain comparable times, 0.55 g of DABCO has to be used.

T_1=20 seconds
T_2=47 seconds
T_3=70 seconds
T_4=90 seconds

EXAMPLE 6

The procedure of Example 2 is repeated using 0.06 g of a catalyst complex of 2-hydrazinopurine/dibutyl tin dilaurate (molar ratio 1:1). The following times are obtained:

T_1=29 seconds
T_2=45 seconds
T_3=46 seconds
T_4=60 seconds

EXAMPLE 7

74 g of catalyst complex of 2-hydrazinopyrimidine/dibutyl tin dilaurate (molar ratio 1:1) are reacted with 11.9 g of phenyl isocyanate in 37 ml of toluene. After 1.5 hours, petroleum ether is added to the suspension formed and the colourless deposit is filtered off under suction. 22 g of N-(2-pyrimidyl)-N'-phenyl semicarbazide melting at 148°C are isolated.

This Example shows that the co-components according to the present invention react off completely in the presence of polyisocyanates to form semicarbazides.

EXAMPLE 8

50 g of a trimethylol-propane-started polyether of 90% of propylene oxide and 10% of ethylene oxide (hydroxyl number 35.4); 1.5 g of water; 0.25 g of a standard commercial-grade silicone stabiliser and 0.25 g of 2-hydrazinopyrimidine/dibutyl tin dilaurate (molar ratio 4:1) are carefully mixed with a high speed stirrer, followed by the addition of 18 g of tolylene diisocyanate (80% of 2,4-isomer and 20% of 2,6-isomer). The mixture is then stirred for another 15 seconds and poured into a card-board dish. Foaming begins after 15 seconds and is over after about 120 seconds. Brief hardening at 80°C completes the gel reaction. An open-cell highly elastic foam is obtained. The density was approximately 35 kg/m^3.

EXAMPLE 9

50 g of a trimethylol-propane-started polyether of 75% of propylene oxide and 25% of ethylene oxide (hydroxyl number=49) are mixed as in Example 8 with 1.75 g of water, 0.25 g of a standard commercial-grade silicone stabiliser, 0.07 g of di-methyl benzylamine and 0.3 g of 2-hydrazinopyrimidine/dibutyl tin dilaurate (molar ratio 4:1), followed by the addition of 42 g of tolylene diisocyanate (80% of 2,4-isomer and 20% of 2,6-isomer). The mixture is stirred for 25 seconds and poured into a mould. Foaming begins after 30 seconds and is complete after 105 seconds. After heating for 10 minutes at 110°C an open-cell elastic foam is obtained.

EXAMPLE 10

A formulation similar to that described in Example 9 is foamed, the only difference being that a polyether of 50% of propylene oxide and 50% of ethylene oxide having a hydroxyl number of 56 is used.

With 41 g of tolylene diisocyanate (80% of 2,4- and 20% of 2,6-isomer), a highly elastic open-cell foam is obtained after a rise time of 115 seconds.

EXAMPLE 11

The procedure is as in Example 10, except that 4-hydrazino-6-methyl pyrimidine is used as the hydrazine component in the catalyst. Using 41 g of tolylene diisocyanate (80% 2,4-isomer content), a highly elastic open-cell foam is obtained after a rise time of 110 seconds.

EXAMPLE 12

The procedure of Example 2 is repeated using 0.06 g of a catalyst complex of 4-hydrazino-6-methyl pyrimidine/dibutyl tin dilaurate (molar ratio 1:1):

T_1=29 seconds
T_2=45 seconds
T_3=48 seconds
T_4=57 seconds.

WHAT WE CLAIM IS:—

1. A catalyst combination for the isocyanate polyaddition reaction consisting of:
(A) 1 mole of a metal compound corresponding to the following general formula:

$$Me\ X_n\ Y_m$$

wherein

Me represents an $(n+m)$ valent metal;

X represents an aliphatic, aromatic or araliphatic hydrocarbon radical;

Y represents an aliphatic carboxylate radical which may contain one or more olefinic double bonds and/or alcoholic hydroxyl groups, an enolate radical, salicylate or naphthenate;

n represents 0, 1 or 2; and

m represents 0 or an integer of from 1 to 4;

provided that the sum $(n+m)$ represents 2, 3 or 4; and

(B) from 0.5 to 6 moles of a heterocyclic aromatic compound which contains at least one tertiary nitrogen atom as hetero-atom and which has at least one hydrazino group as substituent.

2. A catalyst combination as claimed in claim 1 wherein in the general formula of component (A), Me represents a metal selected from: Cu, Ag, Au, Zn, Cd, Hg, Mn, Re, Fe, Co, Ni, Ge, Sn and Pb.

3. A catalyst combination as claimed in claim 1 or claim 2 wherein, in the general formula of component (A), Me represents trivalent iron, divalent nickel, divalent zinc, trivalent manganese, divalent tin or tetravalent tin.

4. A catalyst composition as claimed in any of claims 1 to 3 wherein, in the general formula of component (A), X represents an aliphatic hydrocarbon radical having from 1 to 18 carbon atoms.

5. A catalyst combination as claimed in any of claims 1 to 3 wherein, in the general formula of component (A), X represents an aromatic hydrocarbon radical having from 6 to 10 carbon atoms.

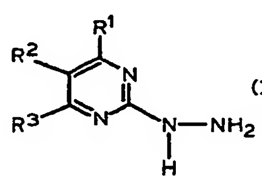
6. A catalyst combination as claimed in any of claims 1 to 3 wherein, in the general formula of component (A), X represents an araliphatic hydrocarbon radical having from 7 to 15 carbon atoms.

7. A catalyst combination as claimed in any of claims 1 to 6 wherein, in the general formula of component (A), Y represents an aliphatic carboxylate radical having from 2 to 18 carbon atoms.

8. A catalyst combination as claimed in any of claims 1 to 6 wherein, in the general formula of component (A), Y represents an enolate radical having from 5 to 18 carbon atoms.

9. A catalyst combination as claimed in any of claims 1 to 8 wherein component (B) is a heterocyclic aromatic compound which has at least one hydrazino group in the ortho- or para-position to the hetero-atom.

10. A catalyst combination as claimed in any of claims 1 to 9 wherein component (B) is a compound corresponding to one of the following general formulae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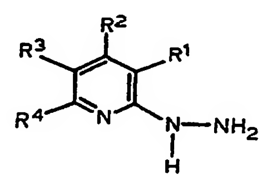
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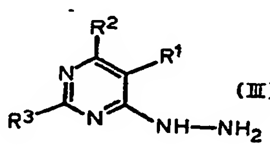
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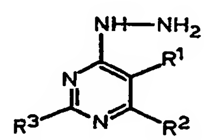
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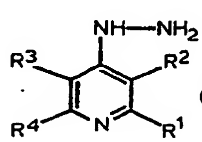
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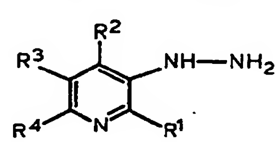
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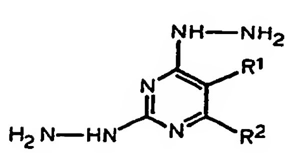
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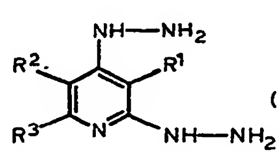
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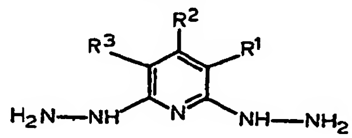

(IX)

wherein

R^1, R^2, R^3 and R^4, which may be the same or different, each represents hydrogen, a hydroxyl, nitro or cyano group, an aliphatic hydrocarbon radical or an aromatic hydrocarbon radical, or R^2 and R^3 or R^1 and R^2 or R^3 and R^4 may also represent a condensed ring.

11. A catalyst combination as claimed in claim 10, wherein, in the general formulae, R^1, R^2, R^3 and/or R^4 each represents an aliphatic hydrocarbon radical containing from 1 to 6 carbon atoms.

12. A catalyst combination as claimed in claim 10 wherein, in the general formulae, R^1, R^2, R^3 and/or R^4 each represents an aromatic hydrocarbon radical containing from 6 to 12 carbon atoms.

13. A catalyst combination as claimed in claim 10 wherein, in the general formulae, R^1, R^2, R^3 and R^4 each represents hydrogen; or one of the radicals R^1 to R^4 represents methyl while each of the others represents hydrogen; or two of the radicals R^1 to R^4 represent a condensed aromatic ring while each of the others represents hydrogen.

14. A catalyst combination as claimed in any of claims 1 to 13 wherein component (B) is 2 - hydrazinopyrimidine; 4 - hydroxy - 2 - hydrazino - 6 - methyl pyrimidine; 2 - hydrazinopurine; 2 - hydrazinopyridine; 2 - hydrazinoquinoline; 5 - nitro - 2-hydrazinopyrimidine; 2 - hydrazino - 6 - methylpyrimidine; 4 - hydrazinopyrimidine; 4 - hydrazino - 6 - methyl pyrimidine; 4 - hydrazino - 6 - phenyl pyrimidine; 6-hydrazino - 2,5 - diphenyl cyanopyrimidine; 3 - hydrazinopyridine; 4 - hydrazino-pyridine; 4 - hydrazinomethyl quinoline; 2 - ethyl - 3 - hydrazinopyridine; 4-hydrazinoquinoline; 2,6 - dihydrazinopyrimidine; 2,6 - dihydrazinopurine; 2,6 - di-hydrazinopyridine or 2,4- and 2,6 - dihydrazinopicoline.

15. A catalyst combination as claimed in claim 1 substantially as herein described.

16. A catalyst combination as claimed in claim 1 substantially as herein described with reference to any one of the Examples.

17. A process for the production of a polyurethane plastics which comprises reacting a polyisocyanate, a compound containing at least two isocyanate-reactive hydrogen atoms and, optionally, a chain-extender in the presence of a catalyst combination as claimed in any of claims 1 to 16.

18. A process as claimed in claim 17 in which the compound containing at least two isocyanate-reactive hydrogen atoms has a molecular weight of from 400 to 10,000.

19. A process as claimed in claim 18 in which the compound containing at least two isocyanate-reactive hydrogen atoms is a polyhydroxyl compound containing from 2 to 8 hydroxyl groups.

20. A process as claimed in claim 19 in which the polyhydroxyl compound has a molecular weight of from 800 to 10,000.

21. A process as claimed in claim 20 in which the polyhydroxyl compound has a molecular weight of from 1000 to 6000.

22. A process as claimed in claim 17 substantially as herein described.

23. A process as claimed in claim 17 substantially as herein described with reference to any one of the Examples.

24. A polyurethane plastics when produced by a process as claimed in any of claims 17 to 23.

ELKINGTON AND FIFE,
Chartered Patent Agents,
High Holborn House,
52/54 High Holborn,
London, WC1V 6SH,
Agents for the Applicants.

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